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(56) Documents Cited
GB 2245584 A GB 2168989 A EP 0398137 A2
US 4873003 A US 4239660 A

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(54) Detergent compositions

(57) There is provided a detergent composition suitable for use in laundry and dish washing methods comprising

(a) a cationic ester surfactant; and

(b) a soil release polymer selected from the group consisting of oligoester soil release polymers and polyamine soil release polymers.

The cationic ester surfactant is preferably a quaternary ammonium compound where one of the alkyl chains is interrupted by an ester-type linkage.

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Detergent compositions

Technical field

The present invention relates to detergent compositions containing a cationic ester surfactant and a soil release polymer which are suitable for use in laundry and dish washing methods.

Background to the invention

The satisfactory removal of greasy soils/stains, that is soils/stains having a high proportion of triglycerides or fatty acids, is a challenge faced by the formulator of detergent compositions for use in laundry and dish washing methods. Surfactant components have traditionally been employed in detergent products to facilitate the removal of such greasy soils/stains. In particular, surfactant systems comprising cationic esters have been described for use in greasy soil/stain removal.

Other detergent components known in the art to facilitate the removal of stains / soils are soil release polymers. During the wash, for example during the sinsing cycle of the wash, soil release polymers adhere to the surface of fabrics by interaction between the fabric and the soil release polymer. Thereby, a polymer layer is formed on the fabric surface, onto which soils can deposit, during the post-wash usage of the fabric. The soil release polymers and attached soils are released from the fabric surface in subsequent wash cycles.

EP-B-21,491 discloses detergent compositions containing a nonionic/cationic surfactant mixture and a builder mixture comprising aluminosilicate and polycarboxylate builder. The cationic surfactant may be

a cationic ester. Improved particulate and greasy/oily soil removal is described.

US-A-4,228,042 discloses biodegradable cationic surfactants, including cationic ester surfactants for use in detergent compositions to provide greasy/oily soil removal. The combination of these cationic surfactants with nonionic surfactants in compositions designed for particulate soil removal is also described.

US-A-4,260,529 discloses laundry detergent compositions having a pH of no greater than 11 containing cationic ester surfactant and nonionic surfactant at defined weight ratios.

It has now been found that the performance of certain soil release polymers in the traditional detergents is affected by the washing conditions, such as water hardness. Essential for the performance of soil release polymers is their affinity for and their deposition onto the fabric. However, deposition onto fabric can be problematic when 'limesoaps' (formed by the alkali and earth alkali metals of the water hardness with fatty acids) are present on the fabric. This problem is believed to cause the reduced performance of certain soil release polymers.

The Applicants have now found that this problem can be ameliorated by inclusion of a cationic ester surfactant in a detergent composition, comprising a polyamine or oligoester soil release polymer. Detergent composition comprising both cationic ester surfactant and such a soil release agent have shown to have a surprisingly better cleaning performance.

Two mechanisms are believed to be responsible for these benefits. Firstly, the cationic ester surfactant can reduce deposition of 'lime soaps' on the fabric. The reduction of 'lime soap' deposition will enable the soil release polymers to adhere to the fabric surface. Secondly, it is believed that the cationic ester surfactant can remove greasy soil/ stain components from the fabric. The removal of greasy stains/soils will enable the soil release polymer to adhere to the fabric surface. Thus, an improvement of their performance is achieved.

All documents cited in the present description are, in relevant part, incorporated herein by reference.

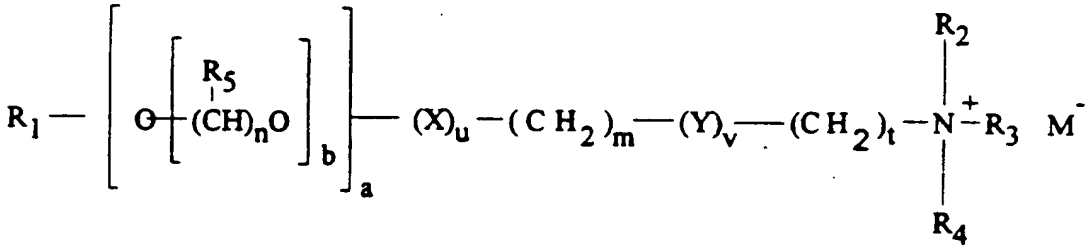
Summary of the Invention

The detergent composition of the present invention comprises

(a) a cationic ester surfactant; and

(b) a soil release polymer selected from the group consisting of oligoester soil release polymers and polyamine soil release polymers.

In a preferred aspect, the cationic ester surfactant is selected from those having the formula:



wherein R_1 is a C_5-C_{31} linear or branched alkyl, alkenyl or alkaryl chain or $M^-.\ N^+(R_6R_7R_8)(CH_2)_s$; X and Y, independently, are selected from the group consisting of COO, OCO, O, CO, OCOO, CONH, NHCO, OCONH and NHCOO wherein at least one of X or Y is a COO, OCO, OCOO, OCONH or NHCOO group; R_2, R_3, R_4, R_6, R_7, and R_8 are independently selected from the group consisting of alkyl, alkenyl, hydroxyalkyl, hydroxy-alkenyl and alkaryl groups having from 1 to 4 carbon atoms; and R_5 is independently H or a C_1-C_3 alkyl group; wherein the values of m, n, s and t independently lie in the range of from 0 to 8, the value of b lies in the range from 0 to 20, and the values of a, u and v independently are either 0 or 1 with the proviso that at least one of u or v must be 1; and wherein M is a counter anion.

Detailed description of the invention

Cationic ester surfactant

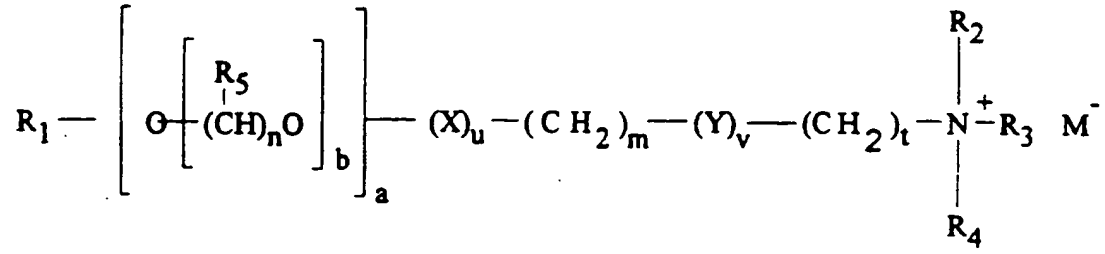
An essential element of the detergent compositions of the invention is a cationic ester surfactant. The cationic ester surfactant is preferably present at a level from 0.1% to 20.0%, more preferably from 0.5% to 10%, most preferably from 1.0% to 5.0% by weight of the detergent composition.

The cationic ester surfactant of the present invention is a, preferably water dispersible, compound having surfactant properties comprising at least one ester (i.e. -COO-) linkage and at least one cationically charged group.

Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

In one preferred aspect the ester linkage and cationically charged group are separated from each other in the surfactant molecule by a spacer group consisting of a chain comprising at least three atoms (i.e. of three atoms chain length), preferably from three to eight atoms, more preferably from three to five atoms, most preferably three atoms. The atoms forming the spacer group chain are selected from the group consisting of carbon, nitrogen and oxygen atoms and any mixtures thereof, with the proviso that any nitrogen or oxygen atom in said chain connects only with carbon atoms in the chain. Thus spacer groups having, for example, -O-O- (i.e. peroxide), -N-N-, and -N-O- linkages are excluded, whilst spacer groups having, for example $-CH_2-O-CH_2-$ and $-CH_2-NH-CH_2-$ linkages are included. In a preferred aspect the spacer group chain comprises only carbon atoms, most preferably the chain is a hydrocarbyl chain.

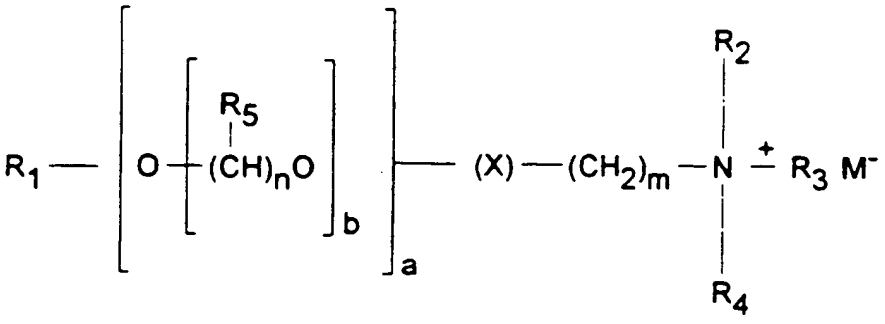
Preferred cationic ester surfactants are those having the formula:



wherein R_1 is a C_5-C_{31} linear or branched alkyl, alkenyl or alkaryl chain or $M^-.N^+(R_6R_7R_8)(CH_2)_s$; X and Y, independently, are selected from the group consisting of COO, OCO, O, CO, OCOO, CONH, NHCO, OCONH and NHCOO wherein at least one of X or Y is a COO, OCO, OCOO, OCONH or NHCOO group; R_2, R_3, R_4, R_6, R_7, and R_8 are independently selected from the group consisting of alkyl, alkenyl, hydroxyalkyl and hydroxy-alkenyl groups having from 1 to 4 carbon atoms and alkaryl groups; and R_5 is independently H or a C_1-C_3 alkyl group; wherein the values of m, n, s and t independently lie in the range of from 0 to 8, the value of b lies in the range from 0 to 20, and the values of a, u and v independently are either 0 or 1 with the proviso that at least one of u or v must be 1; and wherein M is a counter anion.

Preferably M is selected from the group consisting of halide, methyl sulfate, sulfate, and nitrate, more preferably methyl sulfate, chloride, bromide or iodide.

In a preferred aspect, the cationic ester surfactant is selected from those having the formula:

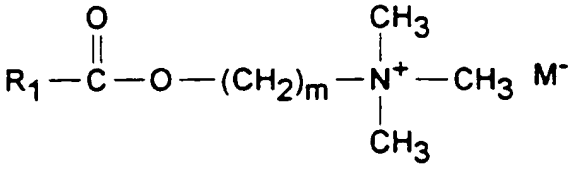


wherein R_1 is a C_5-C_{31} linear or branched alkyl, alkenyl or alkaryl chain; X is selected from the group consisting of COO, OCO, OCOO, OCONH and

NHCOO; R_2, R_3, and R_4 are independently selected from the group consisting of alkyl and hydroxyalkyl groups having from 1 to 4 carbon atoms; and R_5 is independently H or a C_1-C_3 alkyl group; wherein the value of n lies in the range of from 0 to 8, the value of b lies in the range from 0 to 20, the value of a is either 0 or 1, and the value of m is from 3 to 8.

More preferably R_2, R_3 and R_4 are independently selected from a C_1-C_4 alkyl group and a C_1-C_4 hydroxyalkyl group. In one preferred aspect at least one, preferably only one, of R_2, R_3 and R_4 is a hydroxyalkyl group. The hydroxyalkyl preferably has from 1 to 4 carbon atoms, more preferably 2 or 3 carbon atoms, most preferably 2 carbon atoms. In another preferred aspect at least one of R_2, R_3 and R_4 is a C_2-C_3 alkyl group, more preferably two C_2-C_3 alkyl groups are present.

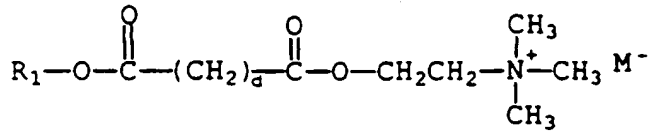
Highly preferred water dispersible cationic ester surfactants are the esters having the formula:

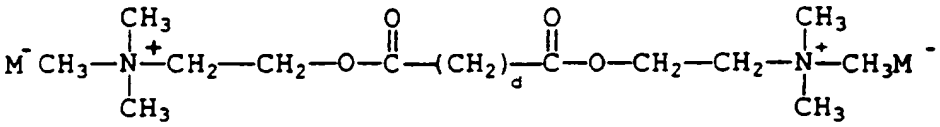


where m is from 1 to 4, preferably 2 or 3 and wherein R_1 is a C_{11}-C_{19} linear or branched alkyl chain.

Particularly preferred choline esters of this type include the stearoyl choline ester quaternary methylammonium halides (R^1=C_{17} alkyl), palmitoyl choline ester quaternary methylammonium halides (R^1=C_{15} alkyl), myristoyl choline ester quaternary methylammonium halides (R^1=C_{13} alkyl), lauroyl choline ester methylammonium halides (R^1=C_{11} alkyl), cocoyl choline ester quaternary methylammonium halides (R^1=C_{11}-C_{13} alkyl), tallowyl choline ester quaternary methylammonium halides (R^1=C_{15}-C_{17} alkyl), and any mixtures thereof.

Other suitable cationic ester surfactants have the structural formulas below, wherein d may be from 0 to 20.





In a preferred aspect the cationic ester surfactant is hydrolysable under the conditions of a laundry wash method.

The particularly preferred choline esters, given above, may be prepared by the direct esterification of a fatty acid of the desired chain length with dimethylaminoethanol, in the presence of an acid catalyst. The reaction product is then quaternized with a methyl halide, preferably in the presence of a solvent such as ethanol, water, propylene glycol or preferably a fatty alcohol ethoxylate such as C_{10}-C_{18} fatty alcohol ethoxylate having a degree of ethoxylation of from 3 to 50 ethoxy groups per mole forming the desired cationic material. They may also be prepared by the direct esterification of a long chain fatty acid of the desired chain length together with 2-haloethanol, in the presence of an acid catalyst material. The reaction product is then quaternized with trimethylamine, forming the desired cationic material.

Soil release polymer

The detergent composition of the invention comprises a soil release polymer, selected from the group consisting of oligoester soil release polymers and polyamine soil release polymers. In accord with the present invention, the oligoester soil release polymers contain an oligoester 'backbone' and the polyamine soil release polymers contain a polyamine (or polyimine) 'backbone'.

The soil release polymers of the present invention are polymeric compounds, which aid soil or stain release from a fabric surface into a wash or cleaning solution. They adhere to the surface of fabrics by interaction between the fabric and the oligoester or polyamine backbone of the

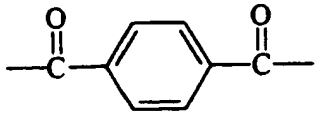
oligoester or polyamine soil release polymers. This occurs when soil release polymers are introduced to a washing/ cleaning process, preferably during the rinsing cycle of a cleaning or washing process. By the adhesion of the soil release polymers to the fabric surface a polymer layer is formed on the fabric surface. This polymer layer adheres to the fabric during optional drying of the fabric after the washing or cleaning process and during post-wash/post-cleaning usage of the fabric. During the usage (and possibly during drying) soils/ stains can deposit onto the polymer layer. In subsequent washing or cleaning cycles the soil release polymer layer and attached soils are released from the fabric surface into the wash or cleaning solution.

Oligoester soil release polymer

A preferred oligoester soil release polymer suitable for use in the detergent compositions of the present invention are those selected from the group of oligoester soil release polymers comprising oligoester soil release polymers containing:

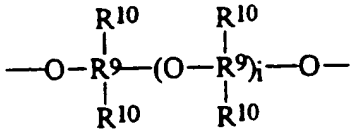
a) a backbone comprising:

i) at least one moiety having the formula:



;

ii) at least one moiety having the formula:



wherein R^9 is C_2-C_6 linear alkylene, C_3-C_6 branched alkylene, C_5-C_7 cyclic alkylene, and mixtures thereof;

R^{10}

is independently selected from hydrogen or -L-$SO_3^-M^+$;

wherein L is a side chain moiety selected from the group consisting of alkylene, oxyalkylene, alkyleneoxyalkylene, arylene, oxyarylene, alkyleneoxyarylene, poly(oxyalkylene), oxyalkyleneoxyarylene, poly(oxyalkylene)oxyarlyene,

alkylenepoly(oxyalkylene),and mixtures thereof; M is hydrogen or a salt forming cation; i has the value of 0 or 1;

iii) at least one trifunctional, ester-forming, branching moiety;

iv) at least one 1,2-oxyalkyleneoxy moiety; and

b) optionally one or more capping units comprising:

i) ethoxylated or propoxylated hydroxyethanesulfonate or ethoxylated or propoxylated hydroxypropanesulfonate units of the formula $(MO_3S)(CH_2)_m(R^{11}O)_n$-, where M is a salt forming cation such as sodium or tetralkylammonium, R^{11} is ethylene or propylene or a mixture thereof, m is 0 or 1, and n is from 1 to 20;

ii) sulfoaroyl units of the formula $-(O)C(C_6H_4)(SO_3^-M^+)$, wherein M is a salt forming cation;

iii) modified poly(oxyethylene)oxy monoalkyl ether units of the formula $R^{12}O(CH_2CH_2O)_k$-, wherein R^{12} contains from 1 to 4 carbon atoms and k is from 3 to 100; and

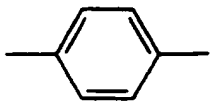
iv) ethoxylated or propoxylated phenolsulfonate end-capping units of the formula $MO_3S(C_6H_4)(OR^{13})_nO$-, wherein n is from 1 to 20; M is a salt-forming cation; and R^{13} is ethylene, propylene and mixtures thereof.

A preferred oligoester soil release polymer of the present invention may be described as having the formula

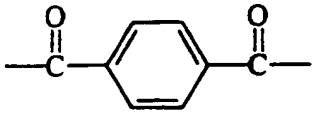
$$[(Cap)(R^4)_t][(A\text{-}R^1\text{-}A\text{-}R^2)_u(A\text{-}R^1\text{-}A\text{-}R^3)_v(A\text{-}R^1\text{-}A\text{-}R^5)_w \text{-}A\text{-}R^1\text{-}A\text{-}][(R^4)_t(Cap)]$$

wherein A is a carboxy linking moiety having the formula

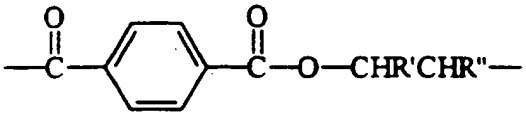
R^1 is arylene, preferably a 1,4-phenylene moiety having the formula



such that when A units and R^1 units are taken together in the formula A-R^1-A they form a terephthalate unit having the formula

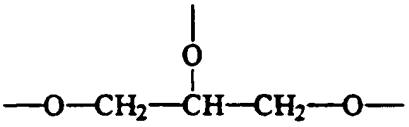


R^2 units are ethyleneoxy or 1,2-propyleneoxy. R^2 units are combined with terephthalate moieties to form (A-R^1-A-R^2) units having the formula

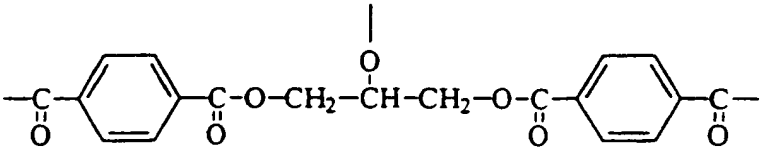


wherein R' and R" are either hydrogen or methyl provided that R' and R" are not both methyl at the same time.

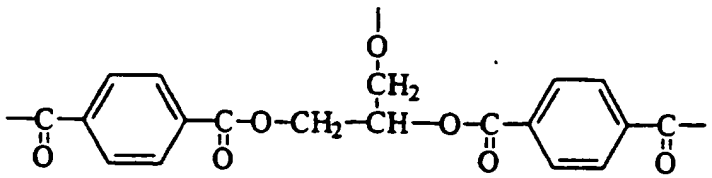
R^3 units are trifunctional, ester-forming, branching moieties having the formula



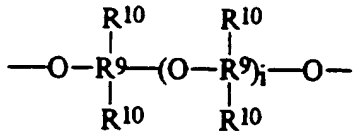
Preferably R^3 units comprise a glycerol moiety which is placed into the soil release polymer backbone to provide a branch point. When R^3 units are combined with terephthalate moieties to form units of the polymer backbone, for example, (A-R^1-A-R^3)-A-R^1-A units, these units have the formula



or the formula

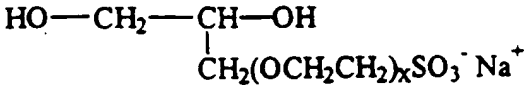


wherein one terephthalate residue is taken to be a part of the (A-R^1-A-R^3) unit while the second terephthalate comprises a part of another backbone unit, such as a (A-R^1-A-R^2) unit, a (A-R^1-A-R^5) unit, a -A-R^1-A-[$(R^4)_t$(Cap)] unit or a second (A-R^1-A-R^3) unit. The third functional group, which is the beginning of the branching chain, is also typically bonded to a terephthalate residue also a part of a (A-R^1-A-R^2) unit, a (A-R^1-A-R^5) unit, a -A-R^1-A-[$(R^4)_t$(Cap)] unit or another (A-R^1-A-R^3) unit.
R^4 units are R^2, R^3 or R^5 units.
R^5 units are units having the formula



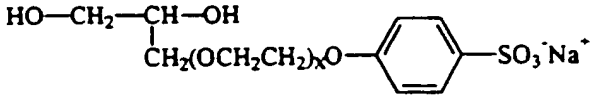
wherein R^9 is C_2-C_6 linear alkylene, C_3-C_6 branched alkylene, and mixtures thereof; preferably R^{10} is independently selected from hydrogen or -L-$SO_3^-M^+$; wherein L is a side chain moiety selected from the group consisting of alkylene, oxyalkylene, alkyleneoxyalkylene, arylene, oxyarylene, alkyleneoxyarylene, poly(oxyalkylene), oxyalkyleneoxyarylene, poly(oxyalkylene)oxyarlyene, alkylenepoly(oxyalkylene),and mixtures thereof; M is hydrogen or a salt forming cation; i has the value of 0 or 1; Each carbon atom of the R^9 units is substituted by R^{10} units that are independently selected from hydrogen or -L-$SO_3^-M^+$, provided no more than one -L-$SO_3^-M^+$ units is attached to an R^9 unit; L is a side chain connecting moiety selected from the group consisting of alkylene, oxyalkylene, alkyleneoxyalkylene, arylene, oxyarylene, alkyleneoxyarylene, poly(oxyalkylene), oxyalkyleneoxyarylene, poly(oxyalkylene)oxyarlyene, alkylenepoly(oxyalkylene),and mixtures thereof.
M is a cationic moiety selected from the group consisting of lithium, sodium, potassium, calcium, and magnesium, preferably sodium and potassium.

The units are easily incorporated into the polymer backbone by using starting materials having the general formula

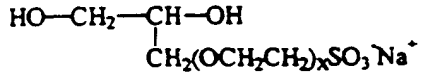


wherein x, for the purposes of the L moiety of the present invention, is from 0 to 20.

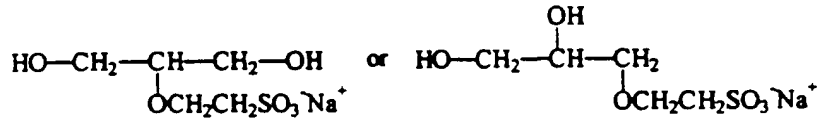
Suitable monomers capable of inclusion into the backbone of this type preferred oligoester soil release polymers of the present invention as R^5 moieties includes the alkylene poly(oxyalkylene)oxyarylene containing monomer having the general formula



wherein x is 0 to 20. A further example of a preferred monomer resulting in a preferred R^5 unit wherein i is equal to 0, are the sodiosulfopoly(ethyleneoxy)methyl-1,2-propanediols having the formula



wherein x is from 0 to about 20; more preferred are the monomers



The preferred soil release agents of the present invention in addition to the afore-mentioned R^1, R^2, R^3, R^4, and R^5 units optionally comprise one or more capping groups, -(Cap). The capping groups are independently selected from ethoxylated or propoxylated hydroxyethane and propanesulfonate units of the formula $(MO_3S)(CH_2)_m(R^AO)_n$-, where M is a salt forming cation such as sodium or tetralkylammonium as described herein above, R^A is ethylene or propylene or a mixture thereof, m is 0 or 1, and n is from 1 to 20, preferably n is from 1 to about 4; sulfoaroyl units of the formula $-(O)C(C_6H_4)(SO_3^-M^+)$, wherein M is a salt forming cation as described herein above; modified poly(oxyethylene)oxy monoalkyl ether units of the formula $R^BO(CH_2CH_2O)_k$- wherein R^B contains from 1 to 4 carbon atoms, R^B is preferably methyl, and k is from 3 to 100, preferably about 3 to 50, more preferably 3 to 30; and ethoxylated or propoxylated

phenolsulfonate end-capping units of the formula $MO_3S(C_6H_4)(OR^C)_nO$- wherein n is from to 20; M is a salt-forming cation; and R^C is ethylene, propylene and mixtures thereof.

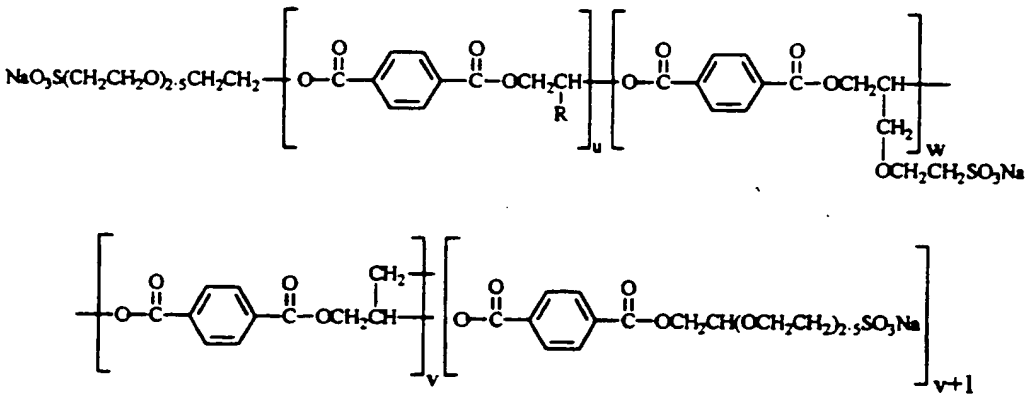
Most preferred end capping unit is the isethionate-type end capping unit which is a hydroxyethane moiety, $(MO_3S)(CH_2)_m(R^AO)_n$-, preferably R^A is ethyl, m is equal to 0, and n is from 2 to 4.

The value of t is 0 or 1; the value of u is from 0 to 60; the value of v is from 0 to 35; the value of w is from 0 to 35.

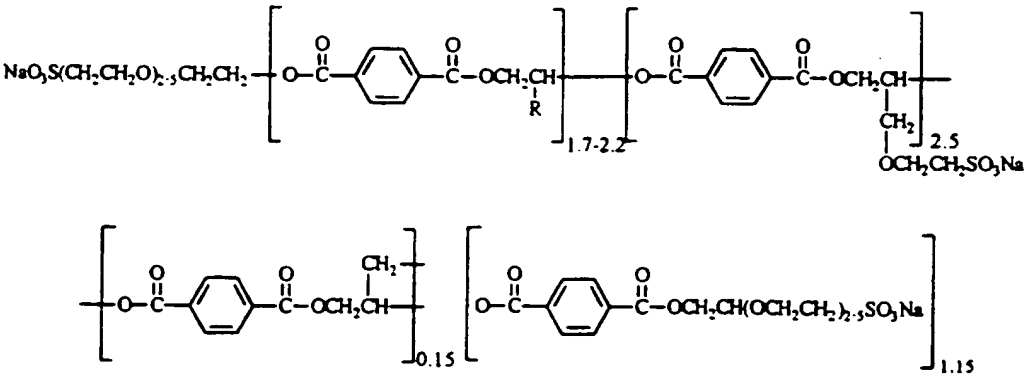
Preferred oligoester soil release polymers of the present invention having the formula

$$[(Cap)(R^4)_t][(A\text{-}R^1\text{-}A\text{-}R^2)_u(A\text{-}R^1\text{-}A\text{-}R^3)_v(A\text{-}R^1\text{-}A\text{-}R^5)_w \text{-}A\text{-}R^1\text{-}A\text{-}][(R^4)_t(Cap)]$$

can be conveniently expressed as the following generic structural formula



The following structure is an example of the preferred oligoester soil release polymers of the present invention.



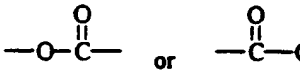
The above-described preferred oligoester soil release agents are fully described in U.S. Patent Application Serial No. 08/545,351 filed November 22, 1995 which is a continuation-in-part of U.S. Patent Application Serial No. 08/355,938 filed December 14, 1994.

Preferred are oligoester soil release polymers of the empirical formula: {(CAP)x(EG/PG)y'(DEG)y"(PEG)y'"(T)z(SIP)z'(SEG)q(B)m} wherein CAP, EG/PG, PEG, T and SIP are as defined as terephthaloyl (T), sulfoisophthaloyl (SIP), oxyethyleneoxy and oxy-1,2-propylene (EG/PG) units, end-caps (CAP), poly(ethyleneglycol) (PEG), (DEG) represents di(oxyethylene)oxy units, (SEG) represents units derived from the sulfoethyl ether of glycerin and related moiety units, (B) represents branching units which are at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone, x is from 1 to 12, y' is from 0.5 to 25, y" is from 0 to 12, y'" is from 0 to 10, y'+y"+y'" totals from 0.5 to 25, z is from 1.5 to 25, z' is from 0 to 12; z + z' totals from about 1.5 to 25, q is from 0.05 to 12; m is from 0.01 to 10, and x, y', y", y'", z, z', q and m represent the average number of moles of the corresponding units per mole of said ester and said ester has a molecular weight ranging from 500 to 5,000. Preferred SEG and CAP monomers for the above oligoester soil release polymers include Na-2-(2-,3-dihydroxypropoxy)ethanesulfonate ("SEG"), Na-2-{2-(2-hydroxyethoxy) ethoxy} ethanesulfonate ("SE3") and its homologs and mixtures thereof and the products of ethoxylating and sulfonating allyl alcohol. Preferred oligoester soil release polymers in this class include the product of transesterifying and oligomerizing sodium 2-{2-(2-hydroxyethoxy)ethoxy}ethanesulfonate and/or sodium 2-[2-{2-(2-hydroxyethoxy)ethoxy}ethoxy]ethanesulfonate, DMT, sodium 2-(2,3-dihydroxypropoxy) ethane sulfonate, EG, and PG using an appropriate Ti(IV) catalyst and can be designated as (CAP)2(T)5(EG/PG)1.4(SEG)2.5(B)0.13 wherein CAP is (Na^+-$O_3S[CH_2$-$CH_2O]_{3.5}$)- and B is a unit from glycerin and the mole ratio EG/PG is about 1.7:1 as measured by conventional gas chromatography after complete hydrolysis.

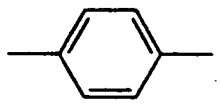
Other highly preferred oligoester soil release polymers are those selected from the class having the formula

$(Cap')[(A'\text{-}R^{11}\text{-}A'\text{-}R^{12})_s(A'\text{-}R^{13}\text{-}A'\text{-}R^{12})_t\text{-}A'\text{-}R^{14}\text{-}A'\text{-}](Cap')$

wherein A' is a carboxy linking moiety, preferably A' is a carboxy linking moiety having the formula



R^{11} is an arylene moiety, preferably 1,4-phenylene moiety having the formula



wherein for R^{11} moieties, the degree of partial substitution with arylene moieties other than 1,4-phenylene should be such that the soil release properties of the compound are not adversely affected to any great extent. Generally, the partial substitution which can be tolerated will depend upon the backbone length of the compound.

R^{12} moieties are ethylene moieties or substituted ethylene moieties having C_1-C_4 alkyl or alkoxy substituents. As used herein, the term "the R^{12} moieties are essentially ethylene moieties or substituted ethylene moieties having C_1-C_4 alkyl or alkoxy substituents" refers to compounds of the present invention where the R^{12} moieties consist entirely of ethylene or substituted ethylene moieties or a partially substituted with other compatible moieties. Examples of these other moieties include 1,3-propylene, 1,4-butylene, 1,5-pentylene, or 1,6-hexylene, 1,2-hydroxyalkylenes and oxyalkylenes.

For the R^{12} moieties, the degree of partial substitution with these other moieties should be such that the soil release properties of the compounds are not adversely affected to any great extent. For example, for polyesters made according to the present invention with a 75:25 mole ratio of diethylene glycol (-$CH_2CH_2OCH_2CH_2$-) to ethylene glycol (ethylene) have adequate soil release activity.

For the R^{13} moieties, suitable substituted C_2-C_{18} hydrocarbylene moieties can include substituted C_2-C_{12} alkylene, alkenylene, arylene, alkarylene and like moieties. The substituted alkylene or alkenylene moieties can be linear, branched or cyclic. Also, the R^{13} can all be the same (e.g. all substituted arylene) or a mixture (e.g. a mixture of substituted arylenes and

substituted alkylenes). Preferred R^{13} moieties are those which are substituted 1,3-phenylene, preferably 5-sulfo-1,3-phenylene. R^{13} moieties are also -A'-[(R^{12}-A'-R^{14})]-Cap' wherein the preferred (Cap') moieties comprise units having the formula

$$—[(R^{15}O)_{m'}(CH_2CH_2O)_{n'}]X$$

wherein R^{15} is C_1-C_4 alkylene, or the moiety -R^{12}-A'-R^{16}- wherein R^{16} is C_2-C_{12} alkylene, alkenylene, arylene or alkarylene moiety, X is C_1-C_4 alkyl, preferably methyl; the indices m' and n' are such that the moiety -CH_2CH_2O- comprises at least 50% by weight of the moiety

$$—[(R^{15}O)_{m'}(CH_2CH_2O)_{n'}]X$$

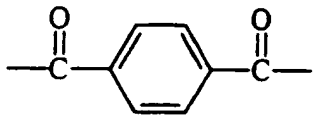
provided that when R^{15} is the moiety -R^{12}-A-R^{16}- , m' is at least 1; each n' is at least 10, the indices s and t are such that the sum of s + t is from 3 to 25.

Other preferred oligoester soil release polymers include sulfonated products of substantially linear ester oligomers comprised of an oligoester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone Such oligo ester soil release polymers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water.

Suitable for use in the laundry detergent compositions of the present invention are preferred oligoester soil release polymers comprising:

a) one or two terminal units selected from the group consisting of
   i) $-(CH_2)_q(CHSO_3M)CH_2SO_3M$,
   ii) $-(CH_2)_q(CHSO_2M)CH_2SO_3M$,
   iii) $-CH_2CH_2SO_3M$,
   iv) and mixtures thereof; wherein q has the value from 1 to about 4, M is a water soluble cation, preferably sodium;

b) a backbone comprising:
   i) arylene units, preferably terephthalate units having the formula:



;

   ii) ethyleneoxy units having the formula:

$$-O(CH_2CH_2O)_nCH_2CH_2O-$$

wherein the value of n is from about 1 to about 20; and

   iii) 1,2-propyleneoxy units having the formula:

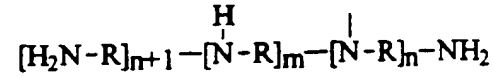
$$-O(CH_2CH(CH_3)O)_nCH_2CH(CH_3)O-$$

wherein the value of n is from 1 to 20, and wherein further the preferred backbone of this preferred non-cotton soil release polymer has a backbone comprising arylene repeat units which alternate with the ethyleneoxy and 1,2-propyleneoxy units, such that the mole ratio of ethyleneoxy to 1,2-propyleneoxy units is from 0:1 to 0.9:0.1, preferably from 0:1 to 0.4:0.6, more preferably the arylene units alternate with essentially 1,2-propyleneoxy units.

Polyamine soil release polymer

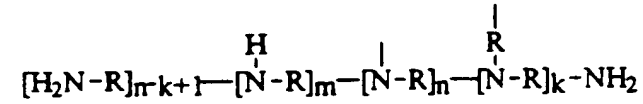
The polyamine soil release polymer of the present invention are water-soluble or dispersible, modified polyamines. These polyamines comprise backbones that can be either linear or cyclic. The polyamine backbones can

also comprise polyamine branching chains to a greater or lesser degree. In general, the polyamine backbones described herein are modified in such a manner that each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, or combinations thereof. For the purposes of the present invention the term "modification" is defined as replacing a backbone -NH hydrogen atom by an E unit (substitution), or quaternizing a backbone nitrogen (quaternized). The terms "modification" and "substitution" are used interchangably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an E unit. Quaternization may take place in some circumstances without substitution. The linear or non-cyclic polyamine backbones that comprise the polyamine soil release polymers of the present invention have the general formula:



said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units.

The cyclic polyamine backbones comprising the polyamine release polymers of the present invention have the general formula:



said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" unit. For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units. For example, when a primary amine moiety, located at the end of the main polyamine backbone or branching chain having the structure

H_2N-R]-

is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure

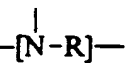
$-NH_2$

is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For example, when a secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure

is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified. These unmodified secondary amine moieties by virtue of their position in the backbone chain remain "backbone" units.

In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, having the structure



is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all or the tertiary amine moieties can remain unmodified. These unmodified tertiary amine moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.

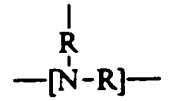
The final modified structure of the polyamine soil release polymers of the present invention can be therefore represented by the general formula

$V_{(n+1)}W_mY_nZ$

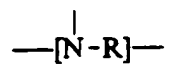
for linear polyamine soil release polymers and by the general formula

$V_{(n-k+1)}W_mY_nY'_kZ$

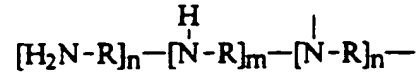
for cyclic polyamine soil release polymers. For the case of polyamines comprising rings, a Y' unit of the formula



serves as a branch point for a backbone or branch ring. For every Y' unit there is a Y unit having the formula



that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula



therefore comprising no Z terminal unit and having the formula

$V_{n-k}W_mY_nY'_k$

wherein k is the number of ring forming branching units. Preferably the polyamine backbones of the present invention comprise no rings.

In the case of non-cyclic polyamines, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified polyamine according to the present invention has the formula

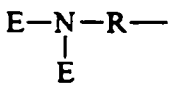
VW_mZ

that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 4 to 400, however larger values of m, especially when the value of the index n is very low or nearly 0, are also preferred.

Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of one of two general classes; simple substituted, or quaternized. Those polyamine nitrogen units not modified are classed into V, W, Y, or Z units depending on whether they are primary, secondary or tertiary nitrogens. That is unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

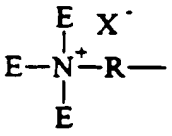
Modified primary amine moieties are defined as V "terminal" units having one of two forms:

a) simple substituted units having the structure:



,

b) quaternized units having the structure:

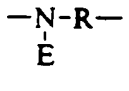


,

wherein X is a suitable counter ion providing charge balance.

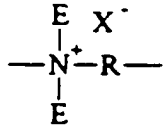
Modified secondary amine moieties are defined as W "backbone" units having one of two forms:

a) simple substituted units having the structure:



,

b) quaternized units having the structure:



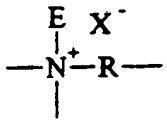
wherein X is a suitable counter ion providing charge balance.

Modified tertiary amine moieties are defined as Y "branching" units having one of two forms:

a) unmodified units having the structure:

,

b) quaternized units having the structure:



,

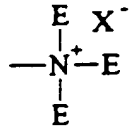
wherein X is a suitable counter ion providing charge balance.

Certain modified primary amine moieties are defined as Z "terminal" units having one of two forms:

a) simple substituted units having the structure:

,

b) quaternized units having the structure:



,

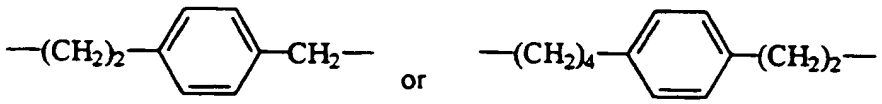
wherein X is a suitable counter ion providing charge balance.

When any position on a nitrogen is unsubstituted of unmodified, it is understood that hydrogen will substitute for E. For example, a primary amine unit comprising one E unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula $(HOCH_2CH_2)HN$-.

For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure $-NH_2$. Non-cyclic polyamine backbones according to the present invention comprise only one Z unit

whereas cyclic polyamines can comprise no Z units. The Z "terminal" unit can be substituted with any of the E units described further herein below.

The polyamine soil release polymers of the present invention comprise backbone R "linking" units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are C_2-C_{12} alkylene, C_4-C_{12} alkenylene, C_3-C_{12} hydroxyalkylene wherein the hydroxyl moiety may take any position on the R unit chain except the carbon atoms directly connected to the polyamine backbone nitrogens; C_4-C_{12} dihydroxyalkylene wherein the hydroxyl moieties may occupy any two of the carbon atoms of the R unit chain except those carbon atoms directly connected to the polyamine backbone nitrogens; C_8-C_{12} dialkylarylene which for the purpose of the present invention are arylene moieties having two alkyl substituent groups as part of the linking chain. For example, a dialkylarylene unit has the formula



although the unit need not be 1,4-substituted, but can also be 1,2 or 1,3 substitutedC_2-C_{12} alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene. The "oxy" R units comprise -$(R^1O)_xR^5(OR^1)_x$-,
-$CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OR^2)CH_2)_w$-,
-$CH_2CH(OR^2)CH_2$-, -$(R^1O)_xR^1$-, and mixtures thereof. Preferred R units are C_2-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxyalkylene, C_8-C_{12} dialkylarylene, -$(R^1O)_xR^1$-, -$CH_2CH(OR^2)CH_2$-, -$(CH_2CH(OH)CH_2O)_z(R^1O)_yR^1(OCH_2CH$-$(OH)CH_2)_w$-, -$(R^1O)_xR^5(OR^1)_x$-, more preferred R units are C_2-C_{12} alkylene, C_3-C_{12} hyc xy-alkylene, C_4-C_{12} dihydroxyalkylene, -$(R^1O)_xR^1$-, -$(R^1 \ _xR^5(OR^1)_x$-,
-$(CH_2CH(OH)CH_2O)_z(R^1O)_yR^1(OCH_2CH$-$(OH)CH_2)_w$-, and mixtures thereof, even more preferred R units are C_2-C_{12} alkylene,
C_3 hydroxyalkylene, and mixtures thereof, most preferred are C_2-C_6 alkylene.
The most preferred backbones of the present invention comprise at least 50% R units that are ethylene.

R^1 units are C_2-C_6 alkylene, and mixtures thereof, preferably ethylene.R^2 is hydrogen, and $-(R^1O)_xB$, preferably hydrogen.
R^3 is C_1-C_{18} alkyl, C_7-C_{12} arylalkylene, C_7-C_{12} alkyl substituted aryl, C_6-C_{12} aryl, and mixtures thereof , preferably C_1-C_{12} alkyl, C_7-C_{12} arylalkylene, more preferably C_1-C_{12} alkyl, most preferably methyl. R^3 units serve as part of E units described herein below.
R^4 is C_1-C_{12} alkylene, C_4-C_{12} alkenylene, C_8-C_{12} arylalkylene, C_6-C_{10} arylene, preferably C_1-C_{10} alkylene, C_8-C_{12} arylalkylene, more preferably C_2-C_8 alkylene, most preferably ethylene or butylene.
R^5 is C_1-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxyalkylene, C_8-C_{12} dialkylarylene, -C(O)-, $-C(O)NHR^6NHC(O)-$, $-C(O)(R^4)_rC(O)-$,
$-R^1(OR^1)-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$,
$-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2-$, R^5 is preferably ethylene, -C(O)-, $-C(O)NHR^6NHC(O)-$, $-R^1(OR^1)-$, $-CH_2CH(OH)CH_2-$,
$-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH-(OH)CH_2-$, more preferably $-CH_2CH(OH)CH_2-$.
R^6 is C_2-C_{12} alkylene or C_6-C_{12} arylene.

The preferred "oxy" R units are further defined in terms of the R^1, R^2, and R^5 units. Preferred "oxy" R units comprise the preferred R^1, R^2, and R^5 units. The preferred polyamine soil release agents of the present invention comprise at least 50% R^1 units that are ethylene. Preferred R^1, R^2, and R^5 units are combined with the "oxy" R units to yield the preferred "oxy" R units in the following manner.

i) Substituting more preferred R^5 into - $(CH_2CH_2O)_xR^5(OCH_2CH_2)_x$- yields - $(CH_2CH_2O)_xCH_2CHOHCH_2(OCH_2CH_2)_x$-.

ii) Substituting preferred R^1 and R^2 into $-(CH_2CH(OR^2)CH_2O)_z$- $(R^1O)_yR^1O(CH_2CH(OR^2)CH_2)_w$- yields - $(CH_2CH(OH)CH_2O)_z$- $(CH_2CH_2O)_yCH_2CH_2O(CH_2CH(OH)CH_2)_w$-.

iii) Substituting preferred R^2 into $-CH_2CH(OR^2)CH_2$- yields

$-CH_2CH(OH)CH_2-$.

E units are selected from the group consisting of hydrogen, C_1-C_{22} alkyl, C_3-C_{22} alkenyl, C_7-C_{22} arylalkyl, C_2-C_{22} hydroxyalkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_mB$, $-C(O)R^3$, preferably hydrogen, C_2-C_{22} hydroxyalkylene, benzyl, C_1-C_{22} alkylene, $-(R^1O)_mB$, $-C(O)R^3$, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, more preferably C_1-C_{22} alkylene, $-(R^1O)_xB$, $-C(O)R^3$, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, most preferably C_1-C_{22} alkylene, $-(R^1O)_xB$, and $-C(O)R^3$. When no modification or substitution is made on a nitrogen then hydrogen atom will remain as the moiety representing E.

B is hydrogen, C_1-C_6 alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q-(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, preferably hydrogen, $-(CH_2)_qSO_3M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q-(CHSO_2M)CH_2SO_3M$, more preferably hydrogen or $-(CH_2)_qSO_3M$.

M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies $-(CH_2)_pCO_2M$, and $-(CH_2)_qSO_3M$, thereby resulting in $-(CH_2)_pCO_2Na$, and $-(CH_2)_qSO_3Na$ moieties. More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the required chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one mono-valent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a $-(CH_2)_pPO_3M$ moiety substituted with sodium atoms has the formula $-(CH_2)_pPO_3Na_3$. Divalent cations such as calcium (Ca^{2+}) or magnesium (Mg^{2+}) may be substituted for or combined with other suitable mono-valent water soluble cations. Preferred cations are sodium and potassium, more preferred is sodium.

X is a water soluble anion such as chlorine (Cl^-), bromine (Br^-) and iodine (I^-) or X can be any negatively charged radical such as sulfate (SO_4^{2-}) and methosulfate ($CH_3SO_3^-$).

The formula indices have the following values: p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1, x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0

or 1; m has the value from 4 to 400, n has the value from 0 to 200; m + n has the value of at least 5.

The most preferred polyamine soil release polymers comprise polyamine backbones wherein less than 50% of the R groups comprise more than 3 carbon atoms. For example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are C_2-C_{12} alkylene, preferred is C_2-C_3 alkylene, most preferred is ethylene.
The polyamine soil release polymers of the present invention comprise modified homogeneous and non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artifact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of polyethyleneimines, therefore a sample of polyethyleneimine that comprises one hydroxyethyl moiety resulting from the polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention. A polyamine backbone comprising all ethylene R units wherein no branching Y units are present is a homogeneous backbone. A polyamine backbone comprising all ethylene R units is a homogeneous backbone regardless of the degree of branching or the number of cyclic branches present.

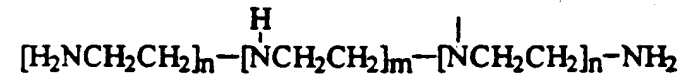
For the purposes of the present invention the term "non-homogeneous polymer backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. For example, a non-homogeneous backbone comprises R units that are a mixture of ethylene and 1,2-

propylene units. For the purposes of the present invention a mixture of "hydrocarbyl" and "oxy" R units is not necessary to provide a non-homogeneous backbone. The proper manipulation of these "R unit chain lengths" provides the formulator with the ability to modify the solubility and fabric substantivity of the soil release agents of the present invention.

Preferred polyamine soil release polymers of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

The preferred polyamine soil release polymers that comprise the backbone of the compounds of the present invention are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's), or PEA's or PEI's connected by moieties having longer R units than the parent PAA's, PAI's, PEA's or PEI's. A common polyalkyleneamine (PAA) is tetrabutylenepentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and teraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.
Preferred amine polymer backbones comprise R units that are C_2 alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1,

however PEI's having a ratio of m to n of 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:



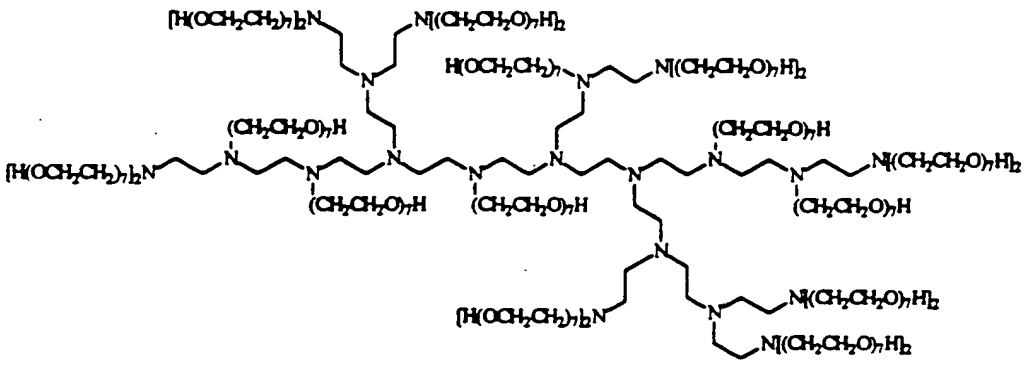
wherein m and n are the same as defined above in this paragraph. Preferred PEI's, prior to modification, will have a molecular weight greater than about 200 daltons.

The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

These polyamine soil release polymers can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951.

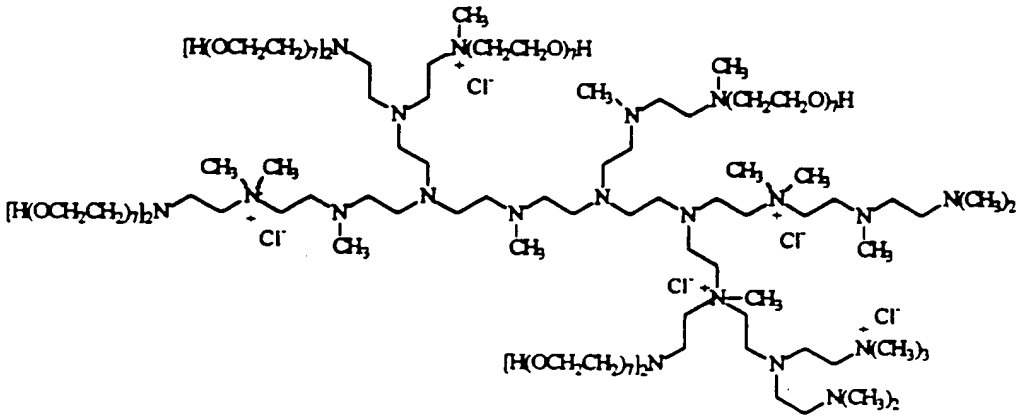
Examples of modified polyamine soil release polymers of the present invention comprising PEI's, are illustrated in Formulas I and II:

Formula I depicts a modified polyamine soil release polymer comprising a PEI backbone wherein all substitutable nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(CH_2CH_2O)_7H$, having the formula



Formula I

Formula II depicts a modified polyamine soil release polymer comprising a PEI backbone wherein all backbone hydrogen atoms are substituted and some backbone amine units are quaternized. The substituents are polyoxyalkyleneoxy units, -$(CH_2CH_2O)_7H$, or methyl groups. The modified PEI cotton soil release polymer has the formula



In the above examples, not all nitrogens of a unit class comprise the same modification. The present invention allows the formulator to have a portion of the secondary amine nitrogens ethoxylated. This also applies to the primary amine nitrogens, in that the formulator may choose to modify all or a portion of the primary amine nitrogens with one or more substituents prior to quaternization. Any possible combination of E groups can be substituted on the primary and secondary amine nitrogens.

Additional detergent components

The detergent compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the precise nature of the washing operation for which it is to be used.

The compositions of the invention preferably contain one or more additional detergent components selected from additional surfactants, bleaches, builders, organic polymeric compounds (not being the polyamines soil release polymers or oligoester soil release polymers of the present invention), additional enzymes, sud suppressors, lime soap dispersants, dye transfer and corrosion inhibitors.

Additional surfactant

The detergent compositions of the invention preferably contain an additional surfactant selected from anionic, nonionic, non-ester cationic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Where present, ampholytic, amphoteric and zwitteronic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

Anionic surfactant

The detergent compositions in accord with the present invention preferably comprise an additional anionic surfactant. Essentially any anionic surfactants

useful for detersive purposes can be comprised in the detergent composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5-C_{17} acyl-N-(C_1-C_4 alkyl) and -N-(C_1-C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C_{10}-C_{18} alkyl sulfates, more preferably the C_{11}-C_{15} branched chain alkyl sulfates and the C_{12}-C_{14} linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C_{10}-C_{18} alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C_{11}-C_{18}, most preferably C_{11}-C_{15} alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C_5-C_{20} linear alkylbenzene sulfonates, alkyl ester sulfonates, C_6-C_{22} primary or secondary alkane sulfonates, C_6-C_{24} olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_2O)_x\ CH_2C00^-M^+$ wherein R is a C_6 to C_{18} alkyl group, x ranges from O to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula $RO-(CHR_1-CHR_2-O)-R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R_3 is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON (R^1) CH_2 COOM, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Alkoxylated nonionic surfactant

Essentially any alkoxylated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

Preferred alkoxylated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

Nonionic alkoxylated alcohol surfactant

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein : R1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C1-C4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1

alkyl (i.e., methyl); and R_2 is a C_5-C_{31} hydrocarbyl, preferably straight-chain C_5-C_{19} alkyl or alkenyl, more preferably straight-chain C_9-C_{17} alkyl or alkenyl, most preferably straight-chain C_{11}-C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

Nonionic fatty acid amide surfactant

Suitable fatty acid amide surfactants include those having the formula: $R^6CON(R^7)_2$ wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and -$(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

Preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)t(glycosyl)_x$$

wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10}-C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

A suitable example of an alkyl aphodicarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C_6-C_{18} hydrocarbyl group, each R^1 is typically C_1-C_3 alkyl, and R^2 is a C_1-C_5 hydrocarbyl group. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10-18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Cationic surfactants

Additional cationic surfactants can also be used in the detergent compositions herein. Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C_6-C_{16}, preferably C_6-C_{10} N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Alkalinity

In the detergent compositions of the present invention preferably a alkalinity system is present to achieve optimal cationic ester surfactant performance. The alkalinity system comprises components capable of providing alkalinity species in solution. By alkalinity species it is meant herein: carbonate, bicarbonate, hydroxide, the various silicate anions, percarbonate, perborates, perphosphates, persulfate and persilicate.
Such alkalinity species can be formed for example, when alkaline salts selected from alkali metal or alkaline earth carbonate, bicarbonate, hydroxide or silicate, including crystalline layered silicate, salts and any mixtures thereof are dissolved in water.

Examples of carbonates are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and any mixtures thereof with ultra-fine calcium carbonate such as are disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Suitable silicates include the water soluble sodium silicates with an SiO_2: Na_2O ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.0 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an SiO_2: Na_2O ratio of 2.0 is the most preferred silicate.

Preferred crystalline layered silicates for use herein have the general formula

$$NaMSi_xO_{2x+1}.yH_2O$$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. Herein, x in the general formula above preferably has a value of 2, 3 or 4 and is preferably 2. The most preferred material is δ-$Na_2Si_2O_5$, available from Hoechst AG as NaSKS-6.

Water-soluble builder compound

The detergent compositions of the present invention preferably contain a water-soluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more that two carbon atoms, borates, phosphates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be momomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in

U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Partially soluble or insoluble builder compound

The detergent compositions of the present invention may contain a partially soluble or insoluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

Examples of largely water insoluble builders include the sodium aluminosilicates.

Suitable aluminosilicate zeolites have the unit cell formula $Na_z[(AlO_2)_z(SiO_2)y]$. xH_2O wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula

$Na_{12}[AlO_2)_{12}(SiO_2)_{12}].xH_2O$

wherein x is from 20 to 30, especially 27. Zeolite X has the formula $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}].276\ H_2O$.

Organic peroxyacid bleaching system

A preferred feature of detergent compositions of the invention is an organic peroxyacid bleaching system. In one preferred execution the bleaching system contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches. In an alternative preferred execution a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

Inorganic perhydrate bleaches

Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the alkali metal, preferably sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain

perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product. Suitable coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps.

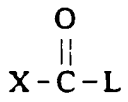
Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$.

Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates herein. Sodium percarbonate is an addition compound having a formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid.

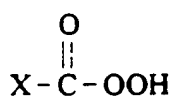
Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

Peroxyacid bleach precursor

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



where L is a leaving group and X is essentially any functionality, such that on perhydroloysis the structure of the peroxyacid produced is



Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by

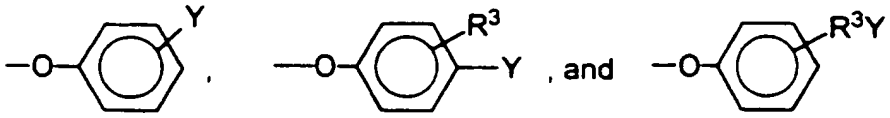
weight, most preferably from 1.5% to 10% by weight of the detergent compositions.

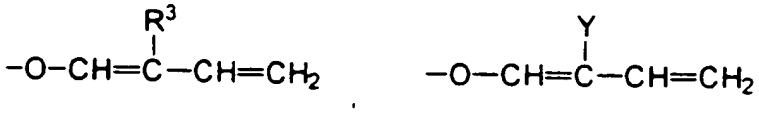
Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

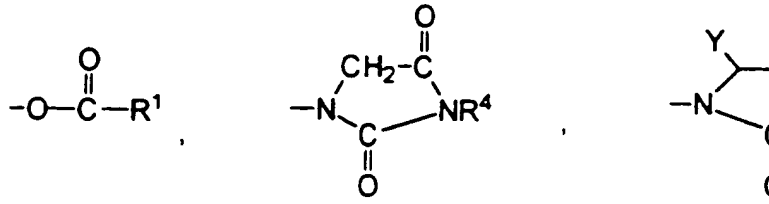
Leaving groups

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:







and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3, and Y is H or a solubilizing group. Any of R^1, R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammmonium groups

The preferred solubilizing groups are $-SO_3^-M^+$, $-CO_2^-M^+$, $-SO_4^-M^+$, $-N^+(R^3)_4X^-$ and $O<-N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Alkyl percarboxylic acid bleach precursors

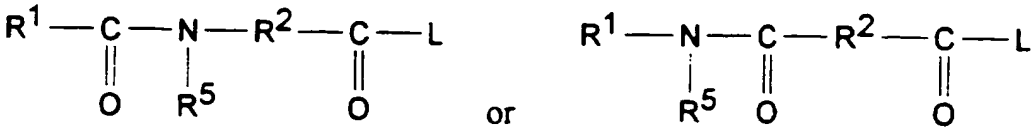
Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

Preferred alkyl percarboxylic precursor compounds of the imide type include the N-,N,N^{1}N^1 tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-trimethyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

Amide substituted alkyl peroxyacid precursors

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:



wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Perbenzoic acid precursor

Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, and the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, and those of the imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole. Other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Cationic peroxyacid precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammmonium group, preferably an ethyl or methyl ammonium group.

Cationic peroxyacid precursors are typically present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter

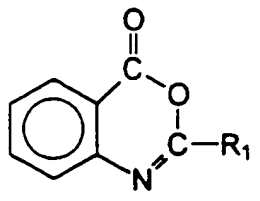
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

Benzoxazin organic peroxyacid precursors

Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

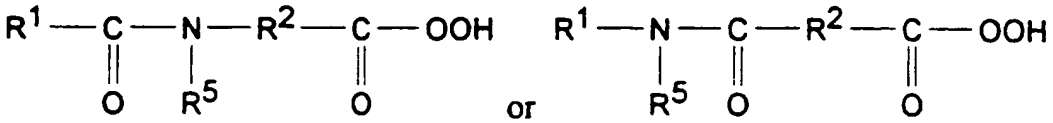


wherein R_1 is H, alkyl, alkaryl, aryl, or arylalkyl.

Preformed organic peroxyacid

The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid , typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R^1 is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid and diperoxyhexadecanedioc acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Bleach catalyst

The compositions optionally contain a transition metal containing bleach catalyst. One suitable type of bleach catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $Mn^{IV}_2(u\text{-}O)_3$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(PF_6)_2$, $Mn^{III}_2(u\text{-}O)_1(u\text{-}OAc)_2$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_2$, $Mn^{IV}_4(u\text{-}O)_6$(1,4,7-triazacyclononane)$_4$-$(ClO_4)_2$, $Mn^{III}Mn^{IV}_4(u\text{-}O)_1(u\text{-}OAc)_2$-(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)$(OCH_3)_3$-(PF_6). Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $N_4Mn^{III}(u\text{-}O)_2Mn^{IV}N_4)^+$and [$Bipy_2Mn^{III}(u\text{-}O)_2Mn^{IV}$bipy$_2$]-$(ClO_4)_3$.

Further suitable bleach catalysts are described, for example, in European patent application No. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Heavy metal ion sequestrant

The detergent compositions of the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in

EP-A-516,102 are also suitable herein. The β-alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are alos suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N-N'-diglutaric acid (EDDG) and 2-hydroxypropylenediamine-N-N'-disuccinic acid (HPDDS) are also suitable.

Enzyme

Another preferred ingredient useful in the detergent compositions is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α-amylases obtained from a special strain of B licheniformis, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold

under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Organic polymeric compound

Organic polymeric compounds are preferred additional components of the detergent compositions in accord with the invention, and are preferably present as components of any particulate components where they may act such as to bind the particulate component together. By organic polymeric compound it is meant herein essentially any polymeric organic compound, not being an oligoester or polyamine soil releasing polymer, and which are commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 100,000, especially 40,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

Suds suppressing system

The detergent compositions of the invention, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C_{18}-C_{40} ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises

(a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination

(i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and

(ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;

wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;

(b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;

(c) an inert carrier fluid compound, most preferably comprising a C_{16}-C_{18} ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon

chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

Polymeric dye transfer inhibiting agents

The detergent compositions herein may additionally comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

The polymeric dye transfer inhibiting agents are preferably selected from copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidonepolymers or combinations thereof.

a) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

Suitable herein are copolymers of N-vinylimidazole and N-vinylpyrrolidone having an average molecular weight range of from 5,000 to 50,000. The preferred copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

b) Polyvinylpyrrolidone

The detergent compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially vailable from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

c) Polyvinyloxazolidone

The detergent compositions herein may also utilize polyvinyloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinyloxazolidones have an average molecular weight of from 2,500 to 400,000.

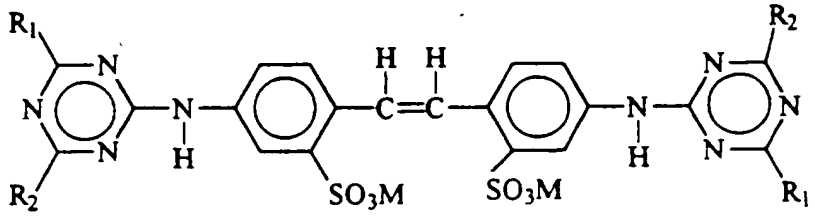
d) Polyvinylimidazole

The detergent compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000.

Optical brightener

The detergent compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation.

Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Other optional ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

pH of the compositions

The present compositions preferably have a pH measured as a 1% solution in distilled water of at least 8.5, preferably from 9.0 to 12.5, most preferably from 9.5 to 11.0.

Form of the compositions

The compositions in accordance with the invention can take a variety of physical forms including granular, tablet, bar and liquid forms. The compositions are particularly the so-called concentrated granular detergent compositions adapted to be added to a washing machine by means of a dispensing device placed in the machine drum with the soiled fabric load.

In general, granular detergent compositions in accordance with the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation.

The mean particle size of the components of granular compositions in accordance with the invention should preferably be such that no more that 5% of particles are greater than 1.7mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

The bulk density of granular detergent compositions in accordance with the present invention typically have a bulk density of at least 600 g/litre, more preferably from 650 g/litre to 1200 g/litre. Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide a bulk density in g/litre. Replicate measurements are made as required.

Surfactant agglomerate particles

The cationic ester surfactant herein, preferably with additional surfactants, is preferably present in granular compositions in the form of surfactant agglomerate particles, which may take the form of flakes, prills, marumes, noodles, ribbons, but preferably take the form of granules. The most preferred way to process the particles is by agglomerating powders (e.g. aluminosilicate, carbonate) with high active surfactant pastes and to control the particle size of the resultant agglomerates within specified limits. Such a process involves mixing an effective amount of powder with a high active surfactant paste in one or more agglomerators such as a pan agglomerator, a Z-blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands, and Gebruder Lodige Maschinenbau GmbH, D-4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050, Germany. Most preferably a high shear mixer is used, such as a Lodige CB (Trade Name).

A high active surfactant paste comprising from 50% by weight to 95% by weight, preferably 70% by weight to 85% by weight of surfactant is typically used. The paste may be pumped into the agglomerator at a temperature high enough to maintain a pumpable viscosity, but low enough to avoid degradation of the anionic surfactants used. An operating temperature of the paste of 50°C to 80°C is typical.

Laundry washing method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

In a preferred use aspect a dispensing device is employed in the washing method. The dispensing device is charged with the detergent product, and is used to introduce the product directly into the drum of the washing machine before the commencement of the wash cycle. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method.

Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its contact with the wash water.

To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Especially preferred dispensing devices for use with the composition of the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a type commonly know as the "granulette". Another preferred dispensing device

for use with the compositions of this invention is disclosed in PCT Patent Application No. WO94/11562.

Especially preferred dispensing devices are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing process. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangemnt to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

Packaging for the compositions

Commercially marketed executions of the bleaching compositions can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates. A preferred packaging execution is described in European Application No. 94921505.7.

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS	:	Sodium linear C_{12} alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
C45AS	:	Sodium C_{14}-C_{15} linear alkyl sulfate
CxyEzS	:	Sodium C_{1x}-C_{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
C45E7	:	A C_{14-15} predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
C25E3	:	A C_{12-15} branched primary alcohol condensed with an average of 3 moles of ethylene oxide
C25E5	:	A C_{12-15} branched primary alcohol condensed with an average of 5 moles of ethylene oxide
CEQ I	:	$R_1COOCH_2.N^+(CH_3)_3$ with $R_1 = C_{11}$-C_{13}
CEQ II	:	$R_1COOCH_2CH_2CH_2N^+(CH_3)_3$ with R_1-C_{11}-C_{13}
CEQ III	:	$R_1COOCH_2CH_2N^+(CH_3)_2(CH_2CH_2OH)$ with R_1=C_{11}-C_{13}
CEQ IV	:	$R_1COOCH_2CH_2N^+R_2R_3(CH_3)$ with R_1=C_{11}-C_{13} and R_2 and R_3=C_2-C_3
QAS	:	$R_2.N^+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_{12}$ - C_{14}
Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils.
TFAA	:	C_{16}-C_{18} alkyl N-methyl glucamide
TPKFA	:	C12-C14 topped whole cut fatty acids
STPP	:	Anhydrous sodium tripolyphosphate
Zeolite A	:	Hydrated Sodium Aluminosilicate of formula $Na_{12}(AlO_2SiO_2)_{12}.27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers
NaSKS-6	:	Crystalline layered silicate of formula δ -$Na_2Si_2O_5$
Citric acid	:	Anhydrous citric acid

Carbonate	:	Anhydrous sodium carbonate with a particle size between 200μm and 900μm
Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm
Silicate	:	Amorphous Sodium Silicate (SiO_2:Na_2O; 2.0 ratio)
Sodium sulfate	:	Anhydrous sodium sulfate
Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425μm and 850μm
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
CMC	:	Sodium carboxymethyl cellulose
Protease	:	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
Alcalase	:	Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S
Cellulase	:	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
Amylase	:	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
Lipase	:	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
Endolase	:	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
PB4	:	Sodium perborate tetrahydrate of nominal formula $NaBO_2.3H_2O.H_2O_2$
PB1	:	Anhydrous sodium perborate bleach of nominal formula $NaBO_2.H_2O_2$
Percarbonate	:	Sodium Percarbonate of nominal formula $2Na_2CO_3.3H_2O_2$
NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt.

TAED	:	Tetraacetylethylenediamine
DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
Photoactivated bleach	:	Sulfonated Zinc Phthlocyanine encapsulated in dextrin soluble polymer
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
HEDP	:	1,1-hydroxyethane diphosphonic acid
PVNO	:	Polyvinylpyridine N-oxide
PVPVI	:	Copolymer of polyvinylpyrolidone and vinylimidazole
SRP 1	:	Sulfobenzoyl end capped esters with oxyethylene oxy and terephtaloyl backbone
SRP 2	:	Diethoxylated poly (1, 2 propylene terephtalate) short block polymer
SRP3	:	Ethoxylated polyethyleneimine with an average molecular weight of 15,000 and with an average of 7 moles of ethylene oxide per nitrogen
Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

In the following Examples all levels are quoted as % by weight of the composition:

Example 1

The following laundry detergent compositions A to F were prepared in accord with the invention:

	A	B	C	D	E	F
LAS	8.0	8.0	8.0	8.0	8.0	8.0

C25E3	3.4	3.4	3.4	3.4	3.4	3.4
CEQ I	0.8	0.8	2.0	2.0	1.0	0.7
CEQ II	0.2	0.5	0.5	2.0	2.6	2.0
QAS	-	-	0.8	-	-	0.8
Zeolite A	18.1	18.1	18.1	18.1	18.1	18.1
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sodium sulfate	26.1	26.1	26.1	26.1	26.1	26.1
PB4	9.0	9.0	9.0	9.0	9.0	9.0
TAED	1.5	1.5.	1.5	1.5	1.5	1.5
DETPMP	0.25	0.25	0.25	0.25	0.25	0.25
HEDP	0.3	0.3	0.3	0.3	0.3	0.3
Protease	0.26	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.1	0.1	0.1	0.1
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
SRP 1	0.5	0.4	-	1.2	3.6	-
SRP 2	0.3	0.4	1.2	-	-	-

SRP 3	0.1	-	1.2	1.2	-	3.9
Photoactivated bleach (ppm)	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

Example 2

The following granular laundry detergent compositions G to I of bulk density 750 g/litre were prepared in accord with the invention:

	G	H	I
LAS	5.25	5.61	4.76
TAS	1.25	1.86	1.57
C45AS	-	2.24	3.89
C25AE3S	-	0.76	1.18
C45E7	3.25	-	5.0
C25E3	-	5.5	-
CEQ I	0.8	2.0	2.0
CEQ III	0.4	1.0	0.5
STPP	19.7	-	-
Zeolite A	-	19.5	19.5
NaSKS-6/citric acid (79:21)	-	10.6	10.6
Carbonate	6.1	21.4	21.4
Bicarbonate	-	2.0	2.0
Silicate	6.8	-	-
Sodium sulfate	39.8	-	14.3

PB4	5.0	12.7	-
TAED	0.5	3.1	-
DETPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
Protease	0.26	0.85	0.85
Lipase	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28
Amylase	0.1	0.1	0.1
MA/AA	0.8	1.6	1.6
CMC	0.2	0.4	0.4
SRP 1	0.4	0.4	0.3
SRP 2	0.4	-	0.5
SRP 3	0.7	1.2	0.8
Photoactivated bleach (ppm)	15 ppm	27 ppm	27 ppm
Brightener 1	0.08	0.19	0.19
Brightener 2	-	0.04	0.04
Perfume	0.3	0.3	0.3
Silicone antifoam	0.5	2.4	2.4

Minors/misc to 100%			

Example 3

The following detergent formulations, according to the present invention were prepared, where J is a phosphorus-containing detergent composition, K is a zeolite-containing detergent composition and L is a compact detergent composition:

	J	K	L
Blown Powder			
STPP	24.0	-	24.0
Zeolite A	-	24.0	-
C45AS	9.0	6.0	13.0
CEQ I	-	2.0	-
CEQ II	-	-	2.0
CEQ III	2.0	-	-
MA/AA	2.0	4.0	2.0
LAS	6.0	8.0	11.0
TAS	2.0	-	-
Silicate	7.0	3.0	3.0
CMC	1.0	1.0	0.5
Brightener 2	0.2	0.2	0.2
Soap	1.0	1.0	1.0
DTPMP	0.4	0.4	0.2
Spray On			
C45E7	2.5	2.5	2.0
C25E3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
Carbonate	6.0	13.0	15.0
PB4	18.0	18.0	10.0
PB1	4.0	4.0	0
TAED	3.0	3.0	1.0
Photoactivated bleach	0.02	0.02	0.02
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.25	0.30	0.15
SRP 1	0.25	-	0.9

SRP 2	0.45	1.2	-
SRP 3	0.3	1.4	1.4
Dry mixed sodium sulfate	3.0	3.0	5.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	630	670	670

Example 4

The following nil bleach-containing detergent formulations of particular use in the washing of colored clothing, according to the present invention were prepared:

	M	N	O
Blown Powder			
Zeolite A	15.0	15.0	-
Sodium sulfate	0.0	5.0	-
LAS	3.0	3.0	-
CEQ I	0.5	0.5	-
CEQ II	1.0	1.5	-
CEQ IV	0.5	1.5	2.5
DTPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Spray On			
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0
Dry additives			
MA/AA	-	-	3.0
NaSKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0	3.0	5.0
Carbonate	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Alcalase	0.5	0.3	0.9
Lipase	0.4	0.4	0.4

Amylase	0.6	0.6	0.6
SRP 1	2.0	-	0.8
SRP 2	-	0.8	-
SRP 3	2.0	1.2	0.9
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	9.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	700	700	700

Example 5

The following detergent formulations, according to the present invention were prepared:

	P	Q	R	S
LAS	20.0	14.0	24.0	22.0
QAS	0.7	1.0	-	0.7
CEQ III	0.4	0.4	2.2	1.5
CEQ IV	1.5	0.4	1.0	1.5
TFAA	-	1.0	-	-
C25E5/C45E7	-	2.0	-	0.5
C45E3S	-	2.5	-	-
STPP	30.0	18.0	30.0	22.0
Silicate	9.0	5.0	10.0	8.0
Carbonate	13.0	7.5	-	5.0
Bicarbonate	-	7.5	-	-
DTPMP	0.7	1.0	-	-
SRP 1	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Protease	0.8	1.0	0.5	0.5
Amylase	0.8	0.4	-	0.25
Lipase	0.2	0.1	0.2	0.1
Cellulase	0.15	0.05	-	-
Photoactivated bleach (ppm)	70ppm	45ppm	-	10ppm
Brightener 1	0.2	0.2	0.08	0.2
PB1	6.0	2.0	-	-
NOBS	2.0	1.0	-	-
SRP 1	-	-	-	0.6
SRP 2	-	-	0.6	-
SRP 3	0.9	2.1	2.2	1.3
Balance (Moisture and Miscellaneous)	100	100	100	100

Example 6

The following detergent formulations, according to the present invention were prepared:

	T	U	V
Blown Powder			
Zeolite A	30.0	22.0	6.0
Sodium sulfate	19.0	5.0	7.0
MA/AA	3.0	3.0	6.0
LAS	14.0	12.0	22.0
C45AS	8.0	7.0	7.0
CEQ II	-	0.4	3.5
CEQ IV	1.5	1.5	-
Silicate	-	1.0	5.0
Soap	-	-	2.0
Brightener 1	0.2	0.2	0.2
Carbonate	8.0	16.0	20.0
DTPMP	-	0.4	0.4
Spray On			
C45E7	1.0	1.0	1.0
Dry additives			
PVPVI/PVNO	0.5	0.5	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.1	0.1	0.1
Cellulase	0.1	0.1	0.1
NOBS	-	6.1	4.5
PB1	1.0	5.0	6.0
Sodium sulfate	-	6.0	-
SRP1	0.3	0.4	-
SRP2	-	0.2	0.3
SRP3	0.6	0.8	0.6
Balance (Moisture and Miscellaneous)	100	100	100

Example 7

The following high density and bleach-containing detergent formulations, according to the present invention were prepared:

	W	X	Y
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sodim sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
CEQ II	5.5	0.5	2.7
CEQ III	0.9	1.2	-
DTPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6

Cellulase	0.6	0.6	0.6
SRP_1	-	0.3	0.3
SRP_2	0.3	-	0.3
SRP_3	0.5	0.5	0.3
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	850	850	850

Example 8

The following high density detergent formulations, according to the present invention were prepared:

	Z	AA
Agglomerate		
C45AS	11.0	14.0
CEQ III	1.8	2.2
Zeolite A	15.0	6.0
Carbonate	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DTPMP	0.4	0.4
Spray On		
C25E5	5.0	5.0
Perfume	0.5	0.5
Dry Adds		
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	3.0	1.0
TAED	5.0	7.0
Percarbonate	20.0	20.0
SRP1	0.3	0.3
SRP2	0.3	0.5
SRP3	1.3	0.8
Protease	1.4	1.4
Lipase	0.4	0.4
Cellulase	0.6	0.6
Amylase	0.6	0.6
Silicone antifoam	5.0	5.0
Brightener 1	0.2	0.2
Brightener 2	0.2	-
Balance (Moisture and Miscellaneous)	100	100
Density (g/litre)	850	850

Example 9

The following liquid detergent formulations, according to the present invention were prepared:

	AB	AC	AD	AE	AF	AG	AH	AI
CEQ I	0.4	1.0	0.8	0.4	2.5	2.0	-	3.5
CEQ II	0.6	1.2	0.7	0.4	-	1.2	2.5	-
LAS	10.0	13.0	9.0	-	25.0	-	-	-
C25AS	4.0	1.0	2.0	10.0	-	13.0	18.0	15.0
C25E3S	1.0	-	-	3.0	-	2.0	2.0	4.0
C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0
QAS	-	-	-	-	3.0	1.0	-	-
TPKFA	2.0	-	13.0	2.0	-	15.0	7.0	7.0
Rapeseed fatty acids	-	-	-	5.0	-	-	4.0	4.0
Citric acid	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodecenyl/tetradecenyl succinic acid	12.0	10.0	-	-	15.0	-	-	-
Oleic acid	4.0	2.0	1.0	-	1.0	-	-	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.-
Mono Ethanol Amine	-	-	-	5.0	-	-	9.0	9.0
Tri Ethanol Amine	-	-	8	-	-	-	-	-
NaOH up to pH	8.0	8.0	7.6	7.7	8.0	7.5	8.0	8.2
Ethoxylated tetraethylene pentamine	0.5	-	0.5	0.2	-	-	0.4	0.3
DTPMP	1.0	1.0	0.5	1.0	2.0	1.2	1.0	-
SRP1	0.1	0.5	-	0.5	0.3	0.2	-	0.2
SRP2	0.3	-	0.3	0.1	-	-	0.2	0.1
SRP3	0.4	0.5	1.0	1.2	0.2	0.7	0.9	1.5
PVNO	-	-	-	-	-	-	-	0.10
Protease	0.5	0.5	0.4	0.25	-	0.5	0.3	0.6
Alcalase	-	-	-	-	1.5	-	-	-
Lipase	-	0.10	-	0.01	-	-	0.15	0.15
Amylase	0.25	0.25	0.6	0.5	0.25	0.9	0.6	0.6
Cellulase	-	-	-	0.05	-	-	0.15	0.15
Endolase	-	-	-	0.10	-	-	0.07	-

Boric acid	0.1	0.2	-	2.0	1.0	1.5	2.5	2.5
Na formate	-	-	1.0	-	-	-	-	-
Ca chloride	-	0.015	-	0.01	-	-	-	-
Bentonite clay	-	-	-	-	4.0	4.0	-	-
Suspending clay SD3	-	-	-	-	0.6	0.3	-	-
Balance (Moisture and Miscellaneous)	100	100	100	100	100	100	100	100

CLAIMS

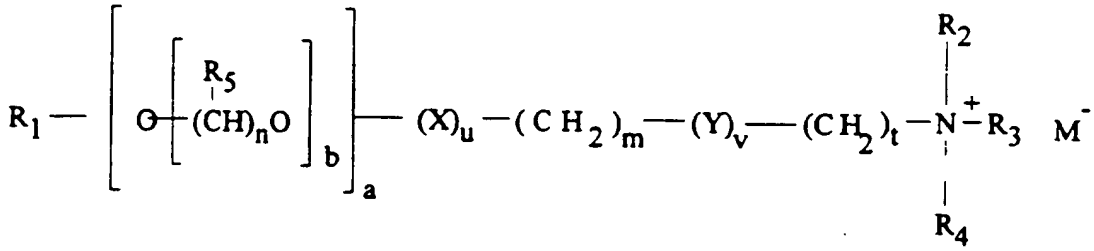
1. A detergent composition comprising

   (a) a cationic ester surfactant; and

   (b) a soil release polymer selected from the group consisting of oligoester soil release polymers and polyamine soil release polymers.

2. A detergent composition according to Claim 1 wherein said cationic ester surfactant is present at a level from 0.5% to 10.0% by weight of said detergent composition.

3. A detergent composition according to either of Claims 1 or 2 wherein the cationic ester surfactant is selected from those having the formula:



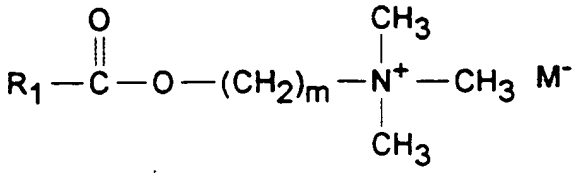
wherein R_1 is a C_5-C_{31} linear or branched alkyl, alkenyl or alkaryl chain or M^-. $N^+(R_6R_7R_8)(CH_2)_s$; X and Y, independently, are selected from the group consisting of COO, OCO, O, CO, OCOO, CONH, NHCO, OCONH and NHCOO wherein at least one of X or Y is a COO, OCO, OCOO, OCONH or NHCOO group; R_2, R_3, R_4, R_6, R_7, and R_8 are independently selected from the group consisting of alkyl, alkenyl, hydroxyalkyl, hydroxy-alkenyl and alkaryl groups having from 1 to 4 carbon atoms; and R_5 is independently H or a C_1-C_3 alkyl group; wherein the values of m, n, s and t independently lie in the range of from 0 to 8, the value of b lies in the range from 0 to 20, and the values of a, u and v independently are either 0 or 1 with the proviso that at least one of u or v must be 1; and wherein M is a counter anion.

4. A detergent composition according to Claim 3 wherein R_2,R_3 and R_4

are independently selected from the group consisting of $-CH_3$ and $-CH_2CH_2OH$.

5. A detergent composition according to Claim 3 wherein both R_2 and R_3 are C_2-C_3 alkyl groups.

6. A detergent composition according to Claim 3 wherein the cationic ester is selected from the choline esters having the formula:



wherein m is from 1 to 4 and R_1 is a C_{11}-C_{19} linear or branched alkyl chain.

7. A detergent composition according to any of Claims 1 to 6 wherein said soil release polymer is present at a level from 0.1% to 15% by weight of the detergent composition.

8. A detergent composition according to any of Claims 1 to 7 wherein said oligoester soil release polymer is of the formula:

$$(Cap')[(A'\text{-}R^{11}\text{-}A'\text{-}R^{12})_s(A'\text{-}R^{13}\text{-}A'\text{-}R^{12})_t\text{-}A'\text{-}R^{14}\text{-}A'\text{-}](Cap')$$

wherein A' is a carboxy linking moiety;
R^{11} is an arylene moiety;
R^{12} are ethylene moieties or substituted ethylene moieties having C_1-C_4 alkyl or alkoxy substituents;
R^{13} are substituted C_2-C_{18} hydrocarbylene moieties;
R^{14} is R^{11} or R^{13} or mixtures thereof.
(Cap') moieties comprise units having the formula

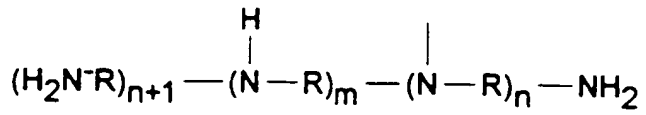
$$—[(R^{15}O)_{m'}(CH_2CH_2O)_{n'}]X$$

wherein R^{15} is C_1-C_4 alkylene, or the moiety -R^{12}-A'-R^{16}- wherein R^{16} is C_2-C_{12} alkylene, alkenylene, arylene or alkarylene moiety, X is C_1-C_4 alkyl, preferably methyl; the indices m and n are such that the moiety -CH_2CH_2O- comprises at least 50% by weight of the moiety

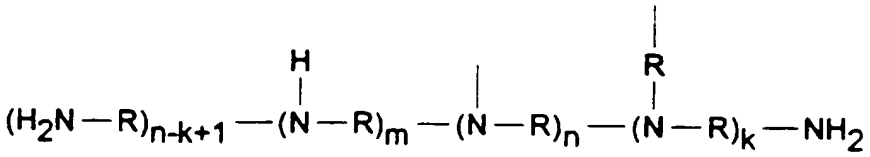
$$—[(R^{15}O)_{m'}(CH_2CH_2O)_{n'}]X$$

provided that when R^{15} is the moiety -R^{12}-A-R^{16}-, m' is at least 1; each n' is at least 10, the indices s and t are such that the sum of s + t is from 3 to 25.

9. A detergent composition according to any of Claims 1 to 7 wherein said polyamine soil release polymer corresponds to the formula:

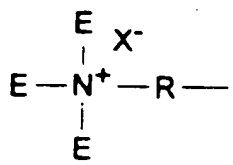


having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone corresponding to the formula:

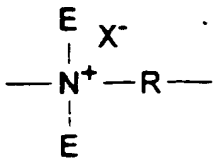


having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n, said polyamine backbone prior to modification has a molecular weight greater than about 200 daltons, wherein

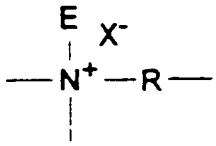
i) V units are terminal units having the formula:



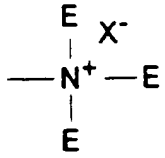
ii) W units are backbone units having the formula:



iii) Y units are branching units having the formula:



iv) Z units are terminal units having the formula:



wherein backbone linking R units are selected from the group consisting of C_2-C_{12} alkylene, $-(R^1O)_xR^3(OR^1)_x-$, $-(CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OR^2)CH_2)_w-$, $-CH_2CH(OR^2)CH_2-$ and mixtures thereof, provided that when R comprises C_1-C_{12} alkylene R also comprises at least one $-(R^1O)_xR^3(OR^1)_x-$, $-(CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1-(OCH_2CH(OR^2)CH_2)_w-$, or $-CH_2CH(OR^2)CH_2-$unit; R^1 is C_2-C6 alkylene and mixtures thereof, R^2 is hydrogen, $-(R^1O)_xB$, and mixtures thereof, R^3 is C_1-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxy-alkylene, C_8-C_{12} dialkylarylene, -C(O)-, $-C(O)NHR^5NHC(O)-$, $-(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2O-(R^1O)_yR^1OCH_2CH(OH)CH_2-$, and mixtures thereof, R^4 is C_1-C_{12} alkylene, C_4-C_{12} alkenylene, C_8-C_{12} arylalkylene, C_6-C_{10} arylene, and mixtures thereof, R^5 is C_2-C_{12} alkylene or C_6-C_{12} arylene; E units are selected from the group consisting of $-(CH_2)_p-CO_2M$,-$(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_xB$, and mixtures thereof; is hydrogen, $-(CH_2)_qSO_3M$, $-(CH_2)_pCH_2M$,

$-(CH_2)_qCH(SO_3M)CH_2SO_3M$, $-(CH_2)_qCH(SO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; k has the value from 0 to about 20; m has the value from 4 to about 400; n has the value from 0 to about 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 to 1.

10. A detergent composition according to Claim 9 wherein R^1 is at least 50% ethylene.

11. A detergent composition according to Claims 9 or 10 wherein R^2 is hydrogen.

12. A detergent composition according to any of Claims 9 to11 wherein R^3 is ethylene, -C(O)-, $-C(O)NHR^6NHC(O)-$, $R^1(OR^1)_y-$, $-(CH_2CH(OH)CH_2O)_z(R^1O)_yR^1-(OCH_2CH(OH)CH_2)_w-$, $-CH_2CH(OH)CH_2-$, or mixtures thereof.

13 A detergent composition according to any of Claims 9-12 wherein R^4 is C_2-C_{12} alkylene, C_8-C_{12} arylalkylene, or mixtures thereof.

14. A detergent composition according to any of Claims 9-13 wherein E units are selected from the group consisting of, $-(R^1O)_xB$, $-(CH_2)_pCO_2-M^+$, $-(CH_2)_qSO_3-M^+$, $-CH(CH_2CO_2M)CO_2M$ and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; p has the value from 1 to 6; x has the value from 1 to 100.

15. A method of washing laundry in a domestic washing machine in which a dispensing device containing an effective amount of a solid detergent composition according to any of Claims 1 to 14 is introduced into the drum of the washing machine before the commencement of the wash, wherein said dispensing device permits progressive release of said detergent composition into the wash liquor during the wash.

The Patent Office

§4

Application No: GB 9611326.1 **Examiner:** Michael Conlon
Claims searched: 1 to15 **Date of search:** 25 September 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C5D (DHC, DHD, DHE, DHZ, DJA, DJX, DEB)

Int Cl (Ed.6): C11D

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
A	GB2245584 A	(Kao)	1
A	GB2168989 A	(Procter & Gamble) page 14 line 25ff	1
A	EP0398137 A2	(Procter & Gamble)	1
A	US4873003	(GAF)	1
X	US4239660	(Procter & Gamble) the examples and column 13 line 18	1

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